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TOXICITY OF PHENYL-MERCURIC LACTATE FOR FISH

by

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Explanatory Note

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INTRODUCTION

Phenyl-mercuric lactate is included in the pulp processing reagents by some paper mills to eliminate slime formation in the pulp. Small quantities of this chemical are added to the wet pulp in the beaters, particularly for the bactericidal action against Aerobacter aerogenes. Subsequently the mercurial is carried away in the wash waters. However, as the highly poisonous nature of many compounds of mercury is well known, questions have been raised concerning the pollution hazards created by phenyl-mercuric lactate in streams receiving effluents from mills using this substance.

The phenyl-mercuric lactate tested in the studies reported here was supplied by Mr. S. J. Post of the Gallowhur Chemical Corporation of New York City. Concerning the sample marked "X-100" Mr. Post makes the following statement:

> Compound X-100 may be described as a phenyl-mercury lactate type formula, toxic in its concentrated form, containing approximately 54.6 percent Hg. as metallic mercury. The product takes the shape of a powder and is readily soluble in water.

BIOASSAYS

In the bioassays and survival tests, six-inch goldfish, Carassius auratus, were used. These fish were in excellent nutritional and metabolic condition and were fully acclimated to the local water. This water is unchlorinated and is very constant in composition. It compares favorably with the common stream waters of central United States, having a specific conductance of 710×10^{-6} at 25° C., an hydrogen-ion concentration of pH 7.7 - 7.8, and is buffered with small but desirable amounts of calcium and carbonates. The total chlorides average about 30 parts per million.

The test fish were carried in individual glass battery jars containing 4 liters of a solution of the test substance. This solution was well aerated and the dissolved oxygen was held between 4 and 6 parts per million. The temperature was maintained at 19° C. (68° F) - 1 degree Centigrade. In general 10 fish or more were carried at each point in the various test series.

In the orientation tests, it was found that 10, 5, 4, 3, 2 and 1 parts per million of the X-100 samples of phenyl-mercuric lactate killed 100 percent of the fish in 7 hours or less and 0.50 parts per million killed all test fish in 16 hours or less. However, there was a 100 percent survival in 0.05 p.p.m.

Studies of various intermediate values between 1 p.p.m. and 0.05 p.p.m. revealed a very sharp break in toxicity below 0.20 p.p.m. The 75 percent lethality value (obtained by graphing the data) is approximately 0.175 p.p.m the 50 percent lethality value 0.15 p.p.m., and the minimal lethal concentration 0.10 p.p.m. for the "X-100" sample of phenyl-mercuric lactate (see Table 1). Although fish gave definite reactions to 0.05 and 0.02 p.p.m. during the first 8 hours of exposure, there was complete survival (the various series were discontinued after 10 days) in all solutions containing 0.05 p.p.m. or less of phenyl-mercuric lactate.

Table 1. Toxicity of phenyl-mercuric lactate to goldfish in a normal water at pH 7.7

Number of fish	Phenyl-mercuric lactate p.p.m.	Percent dead					
		Under 8 hrs.	8-16 hrs.	16-24 hrs.	24-48 hrs.	Over 48 hrs.	Percent surviving 10 days
5	10.00	100	---	---	---	---	---
5	5.00	100	---	---	---	---	---
5	4.00	100	---	---	---	---	---
10	3.00	100	---	---	---	---	---
10	2.00	100	---	---	---	---	---
20	1.00	100	---	---	---	---	---
20	0.50	90	10	---	---	---	---
30	0.20	0	30	60	10	---	---
30	0.15	0	0	50	---	---	50
20	0.10	0	0	20	---	10	70
20	0.05	0	0	0	0	0	100
10	0.02	0	0	0	0	0	100

As the toxicity of some substances, notably ammonium compounds, to fish can be altered by slight changes in pH of the water carrying the toxic it is advisable to determine the toxicity at more than one pH level. In four series each, the water to which the phenyl-mercuric lactate was added was adjusted either to pH 6.3 with hydrochloric acid or pH 9.0 with sodium hydroxide. The points pH 6.3 and pH 9.0 were chosen as pH 6.3 is just above the level at which the acid itself becomes detrimental to fish and pH 9.0 just below the detrimental alkaline level. Control series were maintained in unadjusted water at pH 7.7 and four strengths of phenyl-mercuric lactate tested at each pH level (see Table 2).

Table 2--Toxicity of phenyl-mercuric lactate at different pH levels on goldfish.

Number of fish	Phenyl-mercuric lactate p.p.m.	pH	Percent dead			Percent surviving
			Under 8 hrs.	8-24 hrs.	Over 24 hrs.	
20	0.50	6.3	100	---	---	---
10	"	7.7	90	10	---	---
20	"	9.0	100	---	---	---
20	0.20	6.3	0	100	---	---
10	"	7.7	0	90	10	---
20	"	9.0	0	100	---	---
20	0.10	6.3	0	0	50	50
10	"	7.7	0	20	10	70
20	"	9.0	0	0	50	50
20	0.05	6.3	0	0	0	100
10	"	7.7	0	0	0	100
20	"	9.0	0	0	0	100

A comparison of tables 1 and 2 shows that pH, if within the limits in which pH itself is not a harmful factor, apparently makes no alteration in the toxicity of phenyl-mercuric lactate to fish. The slight differences between the values in table 1 and table 2 were analyzed by statistical methods and found not significant.

PHYSIOLOGICAL ACTION

Fish exposed to phenyl-mercuric lactate in solutions ranging from 0.02 p.p.m. upward showed definite signs of irrigation when first placed in the test solution, swimming rapidly and often making rather erratic movements. After 6 to 8 hours in solutions carrying not more than 0.05 p.p.m. the fish quieted and behaved rather normally, and all signs of distress disappeared in 24 hours or less.

In strengths greater than 0.05 p.p.m. the irritability continued for a longer time but finally disappeared if the fish survived. Those fish which succumbed gradually became lethargic and finally came to rest on the bottom of the jar where they often lived in an almost motionless state for several hours.

In the stronger solutions, that is, those ranging from 0.50 p.p.m. upwards, the stimulation of mucous production was very marked. The mucous covering of the body became partly opaque and turned a bluish white. Usually long strings of more or less coagulated mucus streamed from the gills, the fins and often from the sides of the body. Examination of fish dying in solutions of phenyl-mercuric lactate showed the cause of death to be anoxia due to interference with gill functions by the coagulation films of mucus on the gill filaments and in the gill chambers, in addition to actual damage of the gill filaments. Circulatory failure was hastened also through the mechanical hampering of opercular and gill movements by the masses of partly coagulated mucus. Consequently fish in poorly oxygenated water succumbed more rapidly to phenyl-mercuric lactate than those in well-aerated water.

DISCUSSION

Phenyl-mercuric lactate in view of its chemical composition should fall in the third group of mercury compounds currently recognized by pharmacologists. This group includes the organic mercury compounds in which the mercury is attached more or less firmly to a benzene ring. These poorly ionizable mercurials in general do not precipitate protein and produce slight irritation in contradistinction to the simple highly ionizable inorganic mercury compounds (1) which precipitate and cause marked local irritation. In the experimental tests as noted above, phenyl-mercuric lactate, in spite of its chemical composition, evoked responses in fishes similar to those produced by the highly ionizable inorganic mercury compounds. The phenyl-mercuric lactate did produce local irritation with a marked flow of mucus and did coagulate both the mucus and the tissues of the gills and other exposed portions of the fish's body.

As a check against those observations and also to ascertain the relative toxicity of phenyl-mercuric lactate in terms of its mercury content, series of fish were carried under comparable conditions to those to which the phenyl-mercuric lactate series were exposed, using 1, 0.5 and 0.1 p.p.m. of bichloride of mercury. This compound is the classic example of the highly ionizable inorganic mercurials.

All fish in the 1 p.p.m. and 0.5 p.p.m. series of bichloride of mercury died in 16 to 144 hours, but there was 100 percent survival in the 0.1 p.p.m. series (i.e. ten days, when the series were discontinued). Fish dying in the bichloride of mercury solutions gave the same type of responses as the fish dying in phenyl-mercuric lactate. There was an initial excitement stage, a period of rapid and profuse mucous production, and finally death from anoxia caused by the coagulated mucus on body and gills.

Regardless, therefore, of the chemical structure of phenyl-mercuric lactate, this compound must be listed for fishes at least as an irritant mercurial which caused a profuse flow of mucus and coagulates both mucus and tissues.

As the 50 percent lethality values under the conditions of these studies were approximately 0.25 p.p.m. for bichloride of mercury and 0.15 p.p.m. for phenyl-mercuric lactate, the phenyl-mercuric lactate is definitely more toxic than the inorganic bichloride. When the toxicity is computed on the basis of the amount of mercury present, the greater toxicity of the phenyl-mercuric lactate is even more evident. Bichloride of mercury contains 73.88 percent mercury. Solutions of mercuric bichloride of the 50 percent lethality strength carried, therefore 0.186 milligrams of mercury per liter. Phenyl-mercuric lactate contains 54.7 percent mercury (atomic weights from (2)) and solutions of the 50 percent lethality value carry 0.082 milligrams of mercury per liter. Consequently in terms of contained mercury, the phenyl-mercuric lactate is more than twice as toxic as bichloride of mercury, the ration being 82.186.

It is well known that the toxicity of mercurials is not dependent solely on the mercury content. However, this comparison is made to point out that any evaluation of the pollution hazards of phenyl-mercuric lactate must be based on the reactions of fish and other aquatic life to phenyl-mercuric lactate and not on generalizations concerning the gross amount of mercury involved.

Concerning the dilution required to render the wash waters from the pulp beaters harmless to fish, no final statements can be made until the amount of the phenyl-mercuric lactate leaving the beaters in the wash waters is known, that is, what percent, if any, of the phenyl-mercuric lactate added to the pulp is adsorbed, changed or otherwise removed with the pulp.

In a letter to the writer, Mr. Post states that 1 ounce (presumably avoirdupois) is added to each batch of 15 to 18 tons of wet pulp in the beaters. Assuming that all of the phenyl-mercuric lactate leaves the beaters in the waste water, 74,967 gallons of water would be required to dilute 1 ounce of the phenyl-mercuric lactate to the 0.1 p.p.m. level, which is the minimal lethal concentration found in these studies, and 56,225 gallons of water to dilute one ounce to the 0.15 p.p.m. level which is the 50 percent lethality value for this compound, under conditions reported here.

Two corollaries of the findings in these tests of phenyl-mercuric lactate should be pointed out. It has been noted repeatedly in this laboratory that fish with low respiratory tolerances as trout, various minnows and gizzard shad, succumb to coagulation film anoxia more readily and at higher dissolved oxygen levels than fish with high respiratory tolerances. The goldfish has high respiratory tolerance. Consequently detrimental effects from phenyl-mercuric lactate on fish of the various species having low respiratory tolerances, can be expected at even greater dilutions than the 50 percent lethality value and the minimal lethal concentration as determined for goldfish. Therefore, the species of fish inhabiting the stream into which effluents containing phenyl-mercuric lactate are to be introduced must be known before the maximal amount of phenyl-mercuric lactate likely to be tolerated can be stated.

Throughout these tests on goldfish, the marked bactericidal and bacteriostatic actions of phenyl-mercuric lactate were apparent. This was to be expected as this compound is employed commercially to destroy

Aerobacter aerogens. However, the removal of most bacteria from a stream is undesirable from the fisheries viewpoint as basteria constitute very important basic links in the food chains supporting fish. Mercurials in high dilutions are also very toxic to both algae and infusoria (3), and these two groups include many essential food organisms.

The possible systemic effects of continued exposure to waters carrying phenyl-mercuric lactate in high dilutions is not discussed here as the ten-day periods used in these assays of acutely toxic concentrations were not long enough to yield data on that phase of this problem. However, chronic mercurial poisoning is common in man and mammals (4 and 5) exposed to very small quantities of mercury over long periods of time.

SUMMARY

1. Phenyl-mercuric lactate, although structurally an organic mercury compound, is an irritant mercurial for fish, producing reactions and death similar to those resulting from the highly ionizable inorganic mercurials.

2. Fish exposed to phenyl-mercuric lactate died primarily from anoxia resulting from the coagulation of mucus on the gills and the partial fixation of the gill tissues.

3. The 50 percent lethality value of phenyl-mercuric lactate for goldfish is ± 0.15 perts per million in an average normal water at pH 7.7.

4. The minimal lethal concentration of this compound for goldfish is ± 0.10 p.p.m.

5. The transition from complete lethality to complete survival was very short, lying approximately between 0.20 and 0.05 p.p.m.

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